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Theoretical study on the electronic structures and photophysical properties of a series of dithienylbenzothiazole derivatives

Yan Li [a,b], Lu-Yi Zou [a], Ai-Min Ren [a,*], Ji-Kang Feng [a]

[a] State Key Laboratory of Theoretical and Computational Chemistry, Institute of Theoretical Chemistry, Jilin University, Changchun 130023, China
[b] School of Chemical and Pharmaceutical Engineering, Jilin Institute of Chemical Technology, Jilin 132022, China

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ABSTRACT

Exploring the relationship between electronic structure and electroluminescent property has great significance to design some desirable OLED materials. A series of *dithienylbenzothiazole* derivatives were studied with Density Functional Theory method in this work. The results show that the hole injection/transporting ability of the compound is significantly increased by electron donors (*triphenylamine* and *9-phenylcarbazole*). Introducing the *cyano* group apparently enhances the electron-injection ability of the compound but reduces its hole-injection ability. The *dimethyl-chromene-malononitrile* (*DCM*) group greatly enhances the electron injection/transporting ability of the molecule but has almost no effect on its hole injection/transporting ability. Both the electron reorganization energies and LUMO energy levels of the resulting molecules decrease with increasing electronegativities of the substituents. Extending the π-conjugation length between electron donors and acceptors not only increases the hole/electron injection ability of the molecule, but improves its carrier transport balance.

1. Introduction

Organic light-emitting devices (OLEDs) based on low molecular mass organic materials [1–3] and organic polymers [4,5] have attracted a great deal of attention for the potential use in the next-generation full-color flat-panel displays due to low-cost, easy process and performance improvement. Pure red-emitting molecules and polymers are susceptible to fluorescence quenching in the neat films due to their electronic and structural properties. Based on the current development of OLED materials [6–8], efficient non-doping red-emitters with high visual sensitivity, good electron injection/transporting capability and stability are scarce compared to the other two color light-emitting materials because they are difficult to synthesize, purify and process [9–11]. Recently, small molecular compounds have attracted much interest because of their advantages of reproducibility of synthesis, high purity and definite molecular weight in comparison with their polymer counterparts.

Recently, *2,1,3-benzothiadiazole* has been widely studied as active materials in various optoelectronic devices because it was found to be an important electron acceptor, shown high electron-transporting mobility, and used to construct highly red light emissive materials for potential LED applications [12–14]. Huang et al. have synthesized a new soluble pure red fluorescent molecule *4,7-bis(4-(4-s-butoxyphenyl)-5-(3,5-di(naphthalen-2-yl)phenyl)-thiophen-2-yl)benzo[c][1,2,5]thiadiazole*, named ***a*** (Fig. 1) [15]. And it is demonstrated that it possesses good hole-injection and electron-transporting properties, unlike many other red light-emitting materials, in which hole transport is generally predominant in the solid state. Inspired by the experimental work above, a series of red-light-emitting molecules based on *dithienylbenzothiazole* (*DTBT*) are designed in this work. Chemical structures of substituents including *di(naphthalenyl)benzene* (*DNB*), *triphenylamine* (*TPA*), *9-phenylcarbazole* (*Cy*), *dimethyl-chromene-malononitrile* (*DCM*), *TPA-π-CN*, *Cy-π-CN*, *TPA-π-DCM* and *Cy-π-DCM*, and all designed molecules (named ***b***, ***c***, ***d***, ***e***, ***f***, ***g***, ***h***, ***i***, ***j*** and ***k***) were also shown in Fig. 1. In order to rationalize the experimentally observed properties of known materials and predict those of unknown ones, the various properties of these molecules, such as the highest occupied molecular orbitals (HOMOs), the lowest unoccupied molecular orbitals (LUMOs), HOMO–LUMO gaps (ΔE_{H-L}, the energy difference between the HOMO and LUMO), ionization potentials (IPs), electron affinities (EAs), reorganization energies (λ_s), electronegativities (χ), the lowest excitation energies (E_g), exciton binding energies (E_b), emission energies (E_{Flu}) and fluorescence lifetimes (τ) were investigated theoretically and discussed in detail. In this work, we mainly focus on modulating the electron/hole injection and transporting capacity by different substituents. These results get the underlying relationship between the photophysical property and electroluminescent performance, and will provide constructive information in designing new high-efficiency non-doping red emitting materials.

* Corresponding author. Tel./fax: +86 431 88498567.
E-mail address: aimin_ren@yahoo.com (A.-M. Ren).

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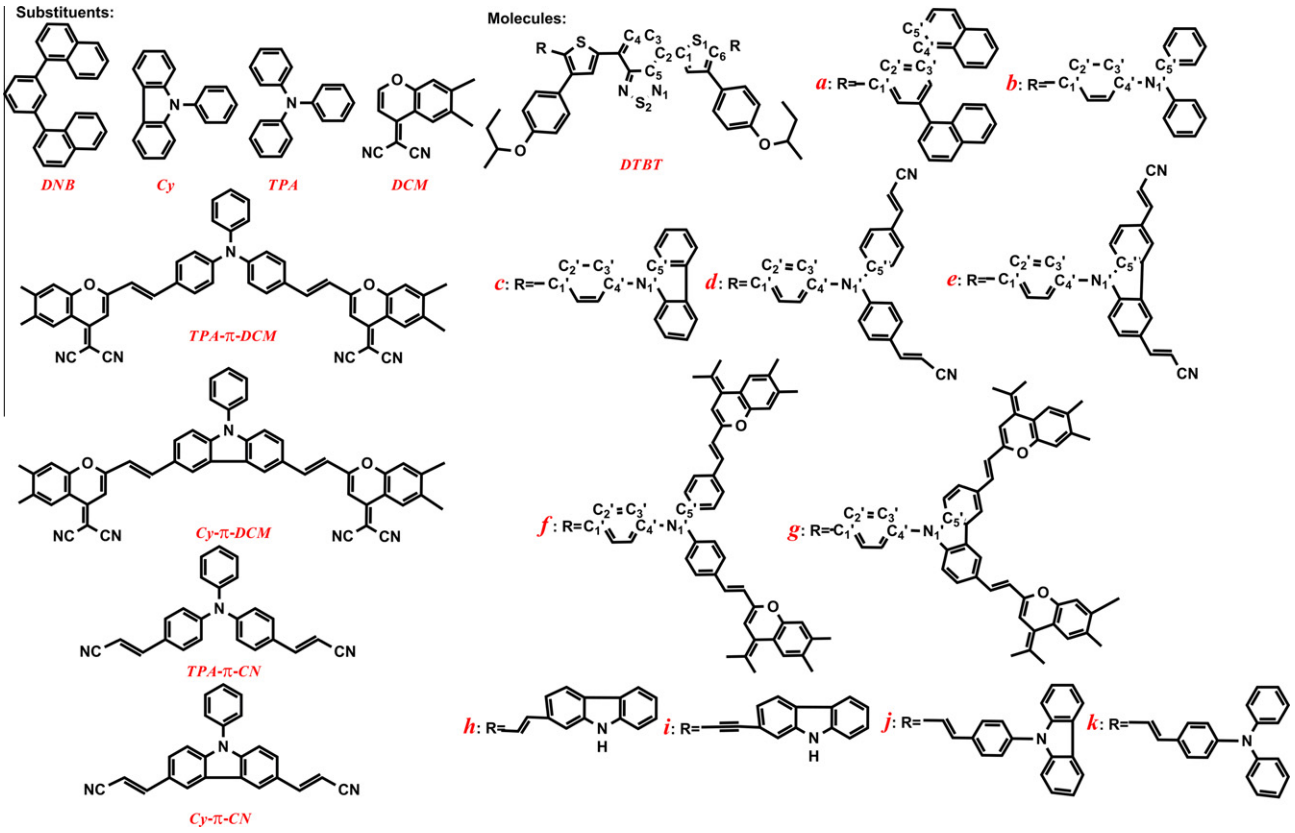

Fig. 1. Sketch map of the structures of ***a–k***.

2. Computational methods and theory

All calculations have been performed with the Gaussian09 package [16] at the Density Functional Theory (DFT) levels with 6-31g* basis set for all atoms.

2.1. Approach selection, geometry optimization and vertical excitation

The ground-state geometry of molecule ***a*** was fully optimized without any symmetry constraints using the Density Functional Theory (DFT) with Becke's three parameter functional and the Lee–Yang–Parr functional (B3LYP) [17] methods. From the optimized ground-state geometry, the absorption spectra were investigated using time-dependent DFT (TD-DFT) calculations [18–20] with several different functional models, such as B3LYP, MPWB1K, MPW1K, BHandHLYP, MPW3LYP, CAM-B3LYP, M062X, M06 and MPW1B95. The solvent (chloroform) effect on the absorption spectra is simulated by means of the Polarizable Continuum Model (PCM). All the results were listed in Table 1, together with the experimental values. It is can be seen from Table 1 that the maximal absorption wavelength (532.5 nm) obtained by TD-MPW1B95//B3LYP is much closer to the experimental data (509 nm) and the solvent effect on it is very small (≈5 nm). Thus, TD-MPW1B95 is particularly efficient to investigate the absorption spectra of molecule ***a*** without taking solvent effect into account. The excited-state geometry of molecule ***a*** was obtained by the configuration interaction with single-excitation (CIS) [21–23], despite the tendency of CIS to overestimate electronic transition energies, the geometry and excited-state potential energy surface can often be quite accurate, as evidenced by comparing excited-state optimizations with experiment data [24–27]. Based on the optimized excited-state geometry, the emission wavelength (634.4 nm) obtained by TD-B3LYP method is very close to the experimental result (622 nm). In this case, the geometries of all the considered molecules in ground and excited state were optimized at the B3LYP and CIS levels without any geometrical restriction, respectively. From the optimized ground- and excited-state geometries, the absorption and emission transition properties were obtained by TD-MPW1B95 and TD-B3LYP levels, respectively.

2.2. Radiative lifetimes

The radiative lifetimes (τ_F) for spontaneous emission can be calculated by using the Einstein transition probabilities according to the following formula (in au) [28,29]:

Table 1
Calculated absorption spectra of ***a*** by different functions, together with experimental values.

a	B3LYP	MPWB1K	MPW1K	BHandHLYP	MPW3LYP	CAM-B3LYP	M062X	M06	MPW1B95	Exp. [15]
λ_{abs} (nm)	587.5 592.4[b]	339.7	462.2	442.5	592.4	443.1	463.3	558.7	532.5	509[a] 491[b]
	371.3 350.1[b]	235.6	305.9	293.8	374.6	295.1	304.8	359.0	343.8	296[a] 294[b]

[a] (in solid).
[b] (in CH_2Cl_2).